

US009129723B2

### (12) United States Patent

#### Wasynczuk

#### (10) **Patent No.:**

US 9,129,723 B2

(45) **Date of Patent:** 

Sep. 8, 2015

### (54) METHOD OF FABRICATING BULK CARBON NANOTUBE AND METALLIC COMPOSITES

(71) Applicant: THE BOEING COMPANY,

Huntington Beach, CA (US)

(72) Inventor: James Antoni Wasynczuk, El Segundo,

CA (US)

(73) Assignee: The Boeing Company, Chicago, IL

(US)

(\*) Notice: Subject to any disclaimer, the term of this

patent is extended or adjusted under 35

U.S.C. 154(b) by 0 days.

(21) Appl. No.: 14/461,760

(22) Filed: Aug. 18, 2014

(65) **Prior Publication Data** 

US 2014/0352869 A1 Dec. 4, 2014

#### Related U.S. Application Data

(62) Division of application No. 13/621,585, filed on Sep. 17, 2012, now Pat. No. 8,865,604.

(51) **Int. Cl.** 

B32B 15/00 (2006.01) D04H 1/00 (2006.01) H01B 1/04 (2006.01) (Continued)

(52) U.S. Cl.

#### (58) Field of Classification Search

CPC .... B82Y 30/00; B82Y 40/00; Y10S 977/742; Y10S 977/75; Y10S 977/752; Y10S 977/842; C01B 2202/02; C01B 2202/08; H01L 21/28556

USPC ............. 977/742, 750–752, 778, 784; 442/59, 442/110–116, 228–231, 316, 317;

428/378–381, 389; 427/123–125, 427/255.28, 250, 431; 156/60, 73.1; 204/192.1

See application file for complete search history.

#### (56) References Cited

#### U.S. PATENT DOCUMENTS

2006/0172179 A1 8/2006 Gu et al. 2009/0008712 A1 1/2009 Choi et al. (Continued)

#### FOREIGN PATENT DOCUMENTS

WO 2010101418 A2 9/2010

OTHER PUBLICATIONS

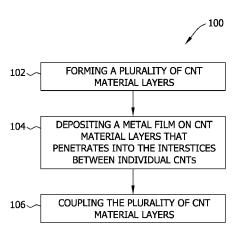
International Search Report and Written Opinion of International Application No. PCT/US2013/049551; Sep. 4, 2013; 9 pages. PCT International Preliminary Report on Patentability for related application PCT/US2013/049551 dated Mar. 17, 2015; 5 p.

Primary Examiner — Matthew Matzek
(74) Attorney, Agent, or Firm — Armstrong Teasdale LLP

#### (57) ABSTRACT

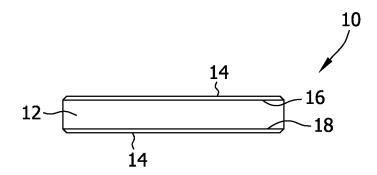
In one embodiment, a bulk carbon nanotube and metallic composite is provided. The bulk carbon nanotube and metallic composite includes a bulk carbon nanotube material layer including a plurality of carbon nanotubes, and a metal film applied across the bulk carbon nanotube material layer. The metal film penetrates into the interstices between individual carbon nanotubes to reduce an electrical resistance between the plurality of carbon nanotubes.

#### 12 Claims, 2 Drawing Sheets



# US 9,129,723 B2 Page 2

(51)	Int. Cl.		(56)	References Cited
	H01B 1/02 R32R 37/06	<b>B32B 37/06</b> (2006.01) <b>C23C 16/06</b> (2006.01)		U.S. PATENT DOCUMENTS
_	C23C 16/06		2009/0035555 2009/0196985	
	C23C 18/54	(2006.01)	2011/0198542	A1 8/2011 Chung et al.



Sep. 8, 2015

FIG. 1

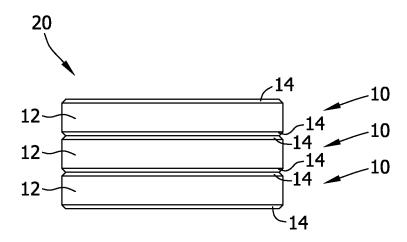


FIG. 2

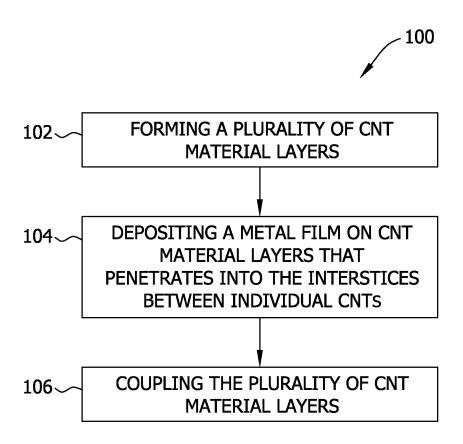


FIG. 3

1

## METHOD OF FABRICATING BULK CARBON NANOTUBE AND METALLIC COMPOSITES

### CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of U.S. patent application Ser. No. 13/621,585, filed Sep. 17, 2012, which is incorporated herein by reference in its entirety.

#### BACKGROUND OF THE DISCLOSURE

The field of the disclosure relates generally to composite materials and, more particularly, to bulk carbon nanotube and metallic composites.

At least some known carbon nanotubes (CNT) are formed from a one-atom thick sheet of graphite commonly referred to as "graphene". The sheet is rolled into a cylinder that has a diameter of the order of a nanometer and a length on the order of a micrometer. Known CNTs exhibit extraordinary strength and electrical properties, and are efficient conductors of heat. The two most common types of CNTs are single-walled carbon nanotubes (SWCNTs) that are formed from a single layer of graphene, and multi-walled carbon nanotubes 25 (MWCNTs) that are formed from multiple concentric cylinders or a graphene sheet that is rolled around itself.

CNTs are lightweight and have a very high elastic modulus. The conductive properties of CNTs depend upon the diameter and the chirality of the hexagonal carbon lattice extending along the tube. A slight change in the winding of the hexagonal lattice along the tube can result in the CNT functioning either as a metal or a semiconductor. For example, hexagonal rows that are parallel to the tube axis produce a metallic structure known as an "armchair" configuration. In contrast, alternating rows of carbon bonds around the tube circumference produce a semi-conducting structure known as a "zigzag" configuration. Although individual CNTs may be highly electrically conductive, high contact resistance between multiple CNTs results in low electrical conductivity of bulk CNT materials.

#### BRIEF DESCRIPTION OF THE DISCLOSURE

In one aspect, a method of fabricating a bulk carbon nanotube and metallic composite is provided. The method includes forming a first bulk carbon nanotube material layer comprising a plurality of carbon nanotubes, and depositing a metal film across the bulk carbon nanotube material layer. The metal film penetrates into the interstices between individual carbon nanotubes to reduce an electrical resistance between the plurality of carbon nanotubes.

In another aspect, a method of fabricating a composite assembly is provided. The method includes forming a first bulk carbon nanotube material layer comprising a plurality of 55 carbon nanotubes, and applying a metal film across an outer surface of the bulk carbon nanotube material layer such that the metal film penetrates through the outer surface and into interstices between individual carbon nanotubes to facilitate reducing an electrical resistance between the plurality of carbon nanotubes. At least a portion of the plurality of carbon nanotubes remain uncoated with the metal film.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is schematic view of an exemplary bulk CNT and metallic composite;

2

FIG. 2 is a schematic view of an exemplary bulk CNT and metallic composite strip; and

FIG. 3 is a block diagram of an exemplary method of fabricating a bulk CNT and metallic composite strip.

### DETAILED DESCRIPTION OF THE DISCLOSURE

FIG. 1 illustrates an exemplary bulk carbon nanotube (CNT) and metallic composite 10 that includes a bulk CNT material layer 12 and one or more thin metal films or layers 14. In the exemplary embodiment, bulk CNT layer 12 includes opposed first and second sides 16 and 18, respectively, and a layer of metal film 14 is deposited across each side 16 and 18. FIG. 2 illustrates an exemplary bulk CNT and metallic composite strip 20 that is fabricated by welding bulk CNT layers 12 together, as will be described in more detail. The methods described herein produce a bulk CNT and metallic composite strip 20 that has a high weight-normalized electrical conductivity, a high thermal conductivity, and a high mechanical strength.

In the exemplary embodiment, bulk CNT layer 12 is fabricated from a plurality of metallic CNTs (not shown), such as "armchair" CNTs, that are each oriented with a chiral angle that is substantially parallel to the tube axis of each CNT. When a graphene sheet (not shown) that forms each CNT is wrapped with an armchair chirality, each formed CNT has an increased metallic character and has an increased capability for tremendously high current density. Alternatively, bulk CNT layer 12 may include a number of semi-conductor CNTs (not shown) in addition to the metallic CNTs. In the exemplary embodiment, bulk CNT layer 12 is a non-woven sheet or a yarn. Alternatively, any other form of bulk CNT layer 12 may be used that enables composite 10 to function as described herein.

In the exemplary embodiment, metal film 14 is applied across CNT layer sides 16 and 18 and penetrates into the interstices between individual CNTs. In the exemplary embodiment, the amount of metal used to form metal film 14 is enough to facilitate low electrical resistance interconnects between a substantial number of the CNTs. In the exemplary embodiment, metal film 14 is a thin-film of aluminum that penetrates the bulk CNT layer 12 and coats a large fraction of the CNTs. Alternatively, metal film 14 may be any electrically conductive metal or combination of metals that enables bulk CNT and metallic composite 10 to function as described herein. In the exemplary embodiment, metal film 14 is applied directly across CNT layer 12 via chemical vapor deposition and/or electroless plating. As such, in the exemplary embodiment, the process facilitates depositing metal within the interstices of the bulk CNT layer. Alternatively, metal film 14 may be applied via a sputtering and/or a physical vapor deposition process. However, any other metal deposition process may be used that enables bulk CNT and metallic composite 10 to function as described herein.

In the exemplary embodiment, multiple bulk CNT and metallic composites 10 are coupled together via a welding process that forms a bulk CNT and metallic composite strip 20. In the exemplary embodiment, and as shown in FIG. 2, three CNT and metallic composites 10 are coupled together along their sides 16 and/or 18. Additionally, CNT and metallic composites 10 may be joined in an end-to-end orientation (not shown). Moreover, any number of CNT and metallic composites 10 may be coupled together to form a bulk CNT and metallic composite strip 20 with any desired length, width and/or thickness. In the exemplary embodiment, CNT and metallic composites 10 are joined together via an ultra-

25

3

sonic welding process. Alternatively, CNT and metallic composites 10 are joined together via an ultrasonic additive manufacturing (UAM) process that sequentially couples layers of patterned metal together to produce net shape products having complex interior cavities.

FIG. 3 illustrates an exemplary method 100 of fabricating a bulk CNT and metallic composite strip 20. Method 100 includes forming 102 a plurality of CNT material layers 12 from a plurality of single-walled carbon nanotubes (SWCNTs) and/or multi-walled carbon nanotubes (MWCNTs). In the exemplary embodiment, CNT material layers 12 are a non-woven sheet or a yarn. The method further includes depositing 104 a metal film 14 across one or more sides 16 and 18 of CNT material layer 12 to form a bulk CNT and metallic composite 10. In the exemplary embodiment, metal film 14 is deposited by at least one of a chemical vapor deposition, an electroless plating, a sputtering, and a physical vapor deposition process. The method also includes coupling 106 multiple bulk CNT and metallic composites 10 together to form a bulk CNT and metallic composite strip 20. In the 20 exemplary embodiment, bulk CNT and metallic composites 10 are coupled together via at least one of an ultrasonic welding and an ultrasonic additive manufacturing process.

#### **EXAMPLE**

In one example, non-woven sheets of bulk CNT material layers 12 are fabricated from individual SWCNTs having a diameter between about 2 nm and about 5 nm, individual MWCNTs having a diameter between about 20 nm and about 30 50 nm, or a combination of both. Each bulk CNT layer 12 is formed with a cross-sectional thickness of between about 20 μm and about 100 μm. A bulk CNT and metallic composite 10 is formed by coating each side 16 and 18 of bulk CNT layer 12 with approximately 3,000 Å (0.3  $\mu$ m) of metallic material. 35 For example, in the exemplary embodiment, a metallic material such as aluminum, copper, nickel, titanium, silver, gold or chromium, or any combination thereof, may be used to form metallic composite 10. Alternatively, any metallic material may be used that enables metallic composite 10 to function as 40 described herein. The resulting bulk CNT and metallic composites 10 are coupled together via an ultrasonic welding process to form a bulk CNT and metallic composite strip 20. The ultrasonic welding process facilitates reducing open space within composites 10 and reducing a thickness of each 45 bulk CNT and metallic composite 10 by approximately 20%. As such, bulk CNT and metallic composite 10 has a decreased electrical resistance between individual CNTs and a decreased electrical resistance. In the example, bulk CNT and metallic composite strip 20 is fabricated with dimensions 50 measuring roughly one cm wide, 10 cm long, and is one to several composites 10 thick.

As described herein, a bulk CNT and metallic composite is fabricated with an increased specific electrical conductivity that is superior to other materials such as copper and aluminum. In addition, the composite exhibits a high electrical conductivity, a high thermal conductivity, and a high mechanical strength. The bulk CNT composite formed with the above techniques reduces contact resistance between individual CNTs and reduced open space within each bulk 60 CNT and metallic composite. Further, a plurality of bulk CNT and metallic composites are coupled to form a high strength, highly electrically conductive bulk CNT and metallic composite strip. The bulk CNT composite material having superior qualities makes it ideal for applications such as EMI 65 shielding, wire conductors for power transmission line, spacecraft harness, and electric motors.

4

This written description uses examples to disclose the various embodiments, including the best mode, and also to enable any person skilled in the art to practice such embodiments, including making and using any devices or systems and performing any incorporated methods. The patentable scope is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

What is claimed is:

1. A method of making a bulk carbon nanotube and metallic composite strip, the method comprising:

forming a first bulk carbon nanotube material layer including a plurality of carbon nanotubes;

depositing a metal film across the bulk carbon nanotube material layer, the metal film penetrating into the interstices between individual carbon nanotubes to reduce an electrical resistance between the plurality of carbon nanotubes to fabricate a first bulk carbon nanotube and metallic composite;

fabricating a second bulk carbon nanotube and metallic composite; and

coupling the first and second bulk carbon nanotube and metallic composites using at least one of an ultrasonic welding process and an ultrasonic additive manufacturing process to form a bulk carbon nanotube and metallic composite strip.

2. The method of claim 1, wherein forming the first bulk carbon nanotube material layer comprises forming at least a portion of the layer using metallic carbon nanotubes.

- 3. The method of claim 1, wherein forming the first bulk carbon nanotube material layer comprises forming at least a portion of the layer using at least one of single-walled carbon nanotubes and multi-walled carbon nanotubes.
- **4**. The method of claim **1**, wherein forming the first bulk carbon nanotube material layer comprises forming at least a portion of the layer using at least one of a non-woven sheet and a yarn.
- 5. The method of claim 1, wherein depositing the metal film comprises applying the metal film onto the bulk carbon nanotube material layer using at least one of a chemical vapor deposition process, an electroless plating process, a sputtering process, and a physical vapor deposition process.
- **6**. The method of claim **1**, wherein depositing the metal film comprises applying at least one of aluminum, nickel, copper, titanium, silver, gold and chromium onto the bulk carbon nanotube material layer.

7. A method of making a bulk carbon nanotube and metallic composite strip, the method comprising:

forming a first bulk carbon nanotube material layer including a plurality of carbon nanotubes;

applying a metal film across an outer surface of the bulk carbon nanotube material layer such that the metal film penetrates through the outer surface and into interstices between individual carbon nanotubes to facilitate reducing an electrical resistance between the plurality of carbon nanotubes, wherein at least a portion of the plurality of carbon nanotubes remain uncoated with the metal film to form a first bulk carbon nanotube and metallic composite;

fabricating a second bulk carbon nanotube and metallic composite; and

coupling the first and second bulk carbon nanotube and metallic composites using at least one of an ultrasonic

6

welding process and an ultrasonic additive manufacturing process to form a bulk carbon nanotube and metallic composite strip.

**8**. The method of claim **7**, wherein forming the first bulk carbon nanotube material layer comprises forming at least a 5 portion of the layer using metallic carbon nanotubes.

5

- 9. The method of claim 7, wherein forming the first bulk carbon nanotube material layer comprises forming at least a portion of the layer using at least one of single-walled carbon nanotubes and multi-walled carbon nanotubes.
- 10. The method of claim 7, wherein forming the first bulk carbon nanotube material layer comprises forming at least a portion of the layer using at least one of a non-woven sheet and a yarn.
- 11. The method of claim 7, wherein depositing the metal 15 film comprises applying the metal film onto the bulk carbon nanotube material layer using at least one of a chemical vapor deposition process, an electroless plating process, a sputtering process, and a physical vapor deposition process.
- 12. The method of claim 7, wherein depositing the metal 20 film comprises applying at least one of aluminum, nickel, copper, titanium, silver, gold and chromium onto the bulk carbon nanotube material layer.

\* \* \* \* \*